

ORIGINAL

Application Based on

Docket **87440AEK**

Inventors: Scott R. Conley

Customer No. 01333

## ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

Commissioner for Patents,  
ATTN: MAIL STOP PATENT APPLICATION  
P.O. Box 1450  
Alexandria, VA. 22313-1450

Express Mail Label No.: EV293530180US

Date: March 18, 2004

## **ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES**

### **FIELD OF THE INVENTION**

This invention relates to an electroluminescent (EL) device comprising a light-emitting layer comprising a boron complex that can provide a range of hues and improved stability.

### **BACKGROUND OF THE INVENTION**

While organic electroluminescent (EL) devices have been known for over two decades, their performance limitations have represented a barrier to many desirable applications. In simplest form, an organic EL device is comprised of an anode for hole injection, a cathode for electron injection, and an organic medium sandwiched between these electrodes to support charge recombination that yields emission of light. These devices are also commonly referred to as organic light-emitting diodes, or OLEDs. Representative of earlier organic EL devices are Gurnee et al. US 3,172,862, issued Mar. 9, 1965; Gurnee US 3,173,050, issued Mar. 9, 1965; Dresner, "Double Injection Electroluminescence in Anthracene", *RCA Review*, 30, 322-334, (1969); and Dresner US 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1  $\mu\text{m}$ ). Consequently, operating voltages were very high, often greater than 100V.

More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g., less than 1.0  $\mu\text{m}$ ) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode. Reducing the thickness lowered the resistance of the organic layer and has enabled devices that operate at much lower voltage. In a basic two-layer EL device structure, described first in US 4,356,429, one organic layer of the EL element adjacent to the anode is specifically chosen to transport holes, and therefore, it is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons, and is referred to as the electron-transporting layer. Recombination of the injected holes and electrons within the organic EL element results in efficient electroluminescence.

There have also been proposed three-layer organic EL devices that contain an organic light-emitting layer (LEL) between the hole-transporting layer and electron-transporting layer, such as that disclosed by Tang et al (*J. Applied Physics*, **65**, Pages 3610-3616, (1989)). The light-emitting layer commonly consists of a host material doped with a guest material, also known as a dopant. Still further, there has been proposed in US 4,769,292 a four-layer EL element comprising a hole-injecting layer (HIL), a hole-transporting layer (HTL), a light-emitting layer (LEL) and an electron transport/injection layer (ETL). These structures have resulted in improved device efficiency.

Since these early inventions, further improvements in device materials have resulted in improved performance in attributes such as color, stability, luminance efficiency and manufacturability, e.g., as disclosed in US 5,061,569, US 5,409,783, US 5,554,450, US 5,593,788, US 5,683,823, US 5,908,581, US 5,928,802, US 6,020,078, and US 6,208,077, amongst others.

Notwithstanding these developments, there are continuing needs for organic EL device components, such as light-emitting materials, sometimes referred to as dopants, that will provide high luminance efficiencies combined with high color purity and long lifetimes. In particular, there is a need to be able to adjust the emission wavelength of the light-emitting material for various applications. For example, in addition to the need for blue, green, and red light-emitting materials there is a need for blue-green, yellow and orange light-emitting materials in order to formulate white-light emitting electroluminescent devices. For example, a device can emit white light by emitting a combination of colors, such as blue-green light and red light or a combination of blue light and orange light.

White EL devices can be used with color filters in full-color display devices. They can also be used with color filters in other multicolor or functional-color display devices. White EL devices for use in such display devices are easy to manufacture, and they produce reliable white light in each pixel of the displays. Although the OLEDs are referred to as white and can appear white or off-white, for this application, the CIE coordinates of the light emitted by the OLED are less

important than the requirement that the spectral components passed by each of the color filters be present with sufficient intensity in that light. The devices must also have good stability in long-term operation. That is, as the devices are operated for extended periods of time, the luminance of the devices should decrease as little as possible. There is a need for new materials that improve the stability of devices.

Ridgidized boron complexes have been used as labeling dyes in analytical and biological applications; for example, see US 4,774,339, EP 747,448 and EP 46, 861. However, boron complexes have found only limited application as dopants in electroluminescent devices. In one example, a useful class of dopants is derived from the 5,6,5-tricyclic pyrromethene-BF<sub>2</sub> complexes and disclosed in US 5,683,823; JP 09 289,081A; and JP 11 097,180A. These materials are characterized by typically narrow emission spectra, which may result in attractively high color purity. However, the green emitting unsubstituted or alkyl substituted pyrromethene-BF<sub>2</sub> complexes exhibit relatively low quantum efficiencies of electroluminescence. In order to achieve highly efficient OLEDs, one needs to use phenyl rings as substituents thereby extending the conjugated  $\pi$ -system. As a result, the emission wavelength typically becomes red-shifted yielding a reddish amber color, which is the shortest wavelength light that can be emitted by pyrromethene-BF<sub>2</sub> complexes with good efficiency. In simple terms, luminance efficient green or blue-green OLEDs do not appear to be conveniently obtained with pyrromethene BF<sub>2</sub> complexes used as dopants.

JP 2001294851A describes boron complexes of heterocycles used in an electroluminescent device. For example, it describes materials in which one ring includes a cyclic amide or sulfonamide. However, these materials are reported to afford a narrow emission spectrum, which would not necessarily be desirable for use in a white-light-emitting device, which must emit a broad spectrum of light. Also, in some cases these materials were not very efficient at emitting light.

US 20030198829A1 and US 20030201415A describe electroluminescent (EL) device containing a boron dopant compound containing a

bis(azinyl)methene boron complex. Such compounds, however, can be inefficient in their quantum efficiency of emission. The use of these materials is also limited by the difficulty in tuning the emission wavelengths, for example, to obtain a blue-green emission.

5                   Bis(phenyloxy)pyridine borohalide complexes have been described by J. Feng, Y Liu, F Li; Y. Wang, S. Liu, *Syn. Met.*, **137**, 1101, (2003), J. Feng, Y Liu, F Li; Y. Wang, S. Liu, *Optical and Quantum Electronics*, **35**, 259 (2003), P. Chou, C. Pi-Tai; C. Cheng, C. Chiou, G. Wu, *Angew. Chem., Int. Ed.*, **41**, 2274, (2002), J. Feng, Y. Liu, Y. Wang, S. Liu, *Chinese Journal of Luminescence*, **23**, 25  
10 (2002), Y. Liu, J. Guo, H. Zhang, Huidong; Y. Wang, *Angew. Chem., Int. Ed.*, **41**, 182, (2002), Y. Li, Y Liu, W. Bu, J. Guo and Y. Wang, *Chem. Comm. (Cambridge)*, **16**, 1551, (2000), and Y. Wang, Y. Wu, L. Yanqin, L. Yu; Lu, J. Shen, *Chinese Patent publication* CN 1245822A. However, in these cases the boron complexes were used to form the entire light-emitting layer and the intensity  
15 of the light emission was not as high as desirable.

                  K. Ueno, K. Suzuki, A. Senoo, H. Tanabe, S. Yogi, EP 1,138,683A2, describe bis(aryloxy)pyridine boroaryl complexes. These materials emit yellow or green light.

                  It is a problem to be solved to provide a material for a light-  
20 emitting layer of an OLED device that exhibits good luminance yield and stability. It is desirable that the material provides a blue or blue-green light emission.

#### **SUMMARY OF THE INVENTION**

                  The invention provides an electroluminescent device comprising a cathode, an anode, and therebetween a layer containing a host material and a  
25 second material comprising a bis(aryloxy)azine borohalide complex. The invention also includes a display device and an area lighting device incorporating the electroluminescent device and a process for emitting light.

                  Embodiments of the invention provide good blue or blue-green light luminance yield and stability.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross-section of a typical OLED device in which this invention may be used.

5

## DETAILED DESCRIPTION OF THE INVENTION

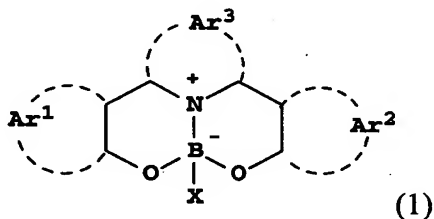
In one embodiment an electroluminescent device of the invention is a multilayer device comprising a cathode, an anode, charge-injecting layers (if necessary), charge-transporting layers, and a light-emitting layer (LEL) comprising a host and at least one light-emitting material. The device includes a layer containing a host material and a second material comprising a bis(aryloxy)azine borohalide complex. In one desirably embodiment, this layer is the light-emitting layer. In one suitable embodiment the layer emits blue or blue-green light. Suitably the bis(aryloxy)azine borohalide complex can comprise a pyridine group and a phenyloxy group. Desirably the complex is a bis(aryloxy)pyridine borofluoro complex.

15

Suitably the bis(aryloxy)azine borohalide complex is present in an amount between 0.5 and 20% by weight of the layer. Typically it is between 0.5 and 8% by weight of the emitting layer.

20

In one desirable embodiment the boron complex is represented by Formula 1.



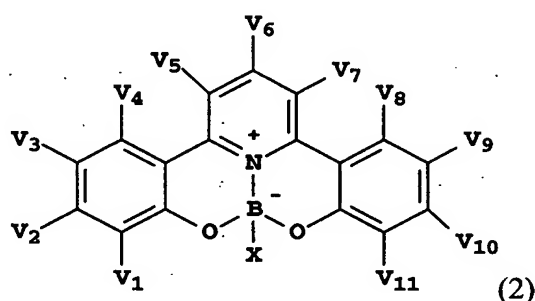
In Formula (1), Ar<sup>1</sup> and Ar<sup>2</sup> independently represent the atoms necessary to form an aromatic ring group, such as a phenyl ring group or a pyridine ring group. Ar<sup>3</sup> represents the atoms necessary to form a six-membered heteroaromatic ring group, such as a pyridine ring group. In addition, Ar<sup>3</sup> and Ar<sup>1</sup> as well as Ar<sup>3</sup> and Ar<sup>2</sup> may join together to form rings. X represents a halide, such as Cl or F. In one desirable embodiment, X represents F.

25

The rings formed by Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> may contain additional fused rings. For example Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> may be fused with independently selected benzene ring groups. In one suitable embodiment the substituents of Formula (1) are chosen so that at least six rings are present.

5 In one suitable embodiment substituents of Formula (1) are selected to prevent or limit exciplex formation. That is, substituents are chosen that inhibit the formation of excited state complexes involving one or more compounds of Formula (1). Particularly useful substituents introduce steric interactions, such as one or more *t*-butyl groups, *s*-pentyl groups, or mesityl groups.  
10 groups.

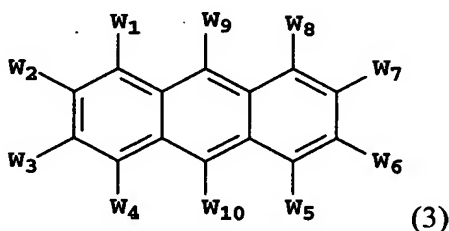
In one desirable embodiment Formula (2) represents the boron complex.



In Formula (2), each V<sub>1</sub> – V<sub>11</sub> represents hydrogen or an  
15 independently selected substituent, provided that substituents may combine to form rings. For example, V<sub>1</sub> – V<sub>11</sub> may independently represent phenyl groups or fuse together to form naphthyl groups. X represents a halide. Desirably X represents F.

Desirable hosts include those based on an anthracene compound.

20 In one desirable embodiment the host is represented by Formula (3).



In Formula (3), each of  $W_1$ - $W_{10}$  represents hydrogen or an independently selected substituent, provided that two substituents can combine to form rings. In one suitable embodiment,  $W^9$  and  $W^{10}$  independently represent naphthyl groups. In another desirable embodiment,  $W^9$  and  $W^{10}$  represent a  
5 naphthyl group and a biphenyl group.

Particular examples of hosts are 9,10-di-(2-naphthyl)anthracene, 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene, 9-(4-biphenyl)-10-(2-naphthyl)anthracene and 9-(4-biphenyl)-10-(1-naphthyl)anthracene. Preferably, the host is selected such that the host absorbs light at a shorter wavelength than the dopant and the  
10 emission spectrum of the host overlaps with the absorption spectrum of the dopant.

Embodiments of the light-emitting materials useful in the invention can provide a range of hues. Embodiments of the light-emitting materials especially useful in the invention provide an emitted light having a blue hue or  
15 blue-green hue. In another preferred embodiment, light-emitting materials useful in the invention are used in an electroluminescent device that emits white light.

In one embodiment, the light-emitting layer contains, in addition to the host and the bis(aryloxy)azine borohalide complex at least one additional material (a third material) which emits light. In this case the bis(aryloxy)azine  
20 borohalide complex can act to improve the operational stability of the device. In one embodiment this additional material emits blue light. In one embodiment the bis(aryloxy)azine borohalide complex does not emit light.

Suitably the third material is present in an amount between 0.5 and 20% by weight of the light-layer. Typically it is between 0.5 and 8% by weight of  
25 the light-emitting layer.

A particularly useful class of light-emitting material includes perylene and its derivatives such as a perylene nucleus bearing one or more substituents such as an alkyl group or an aryl group. A desirable perylene  
derivative for use as a blue emitting material is 2,5,8,11-tetra-*t*-butylperylene.

30 Another useful class of light-emitting materials includes blue-light emitting derivatives of distyrylarenes such as distyrylbenzene and

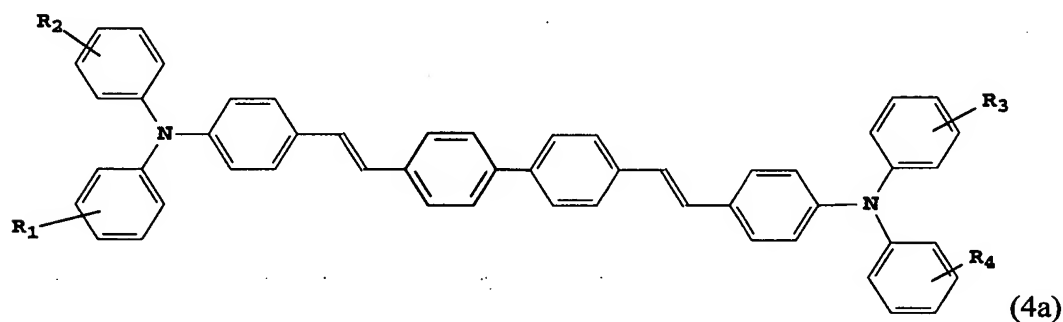


distyrylbiphenyl, including compounds described in U.S. Patent 5,121,029.

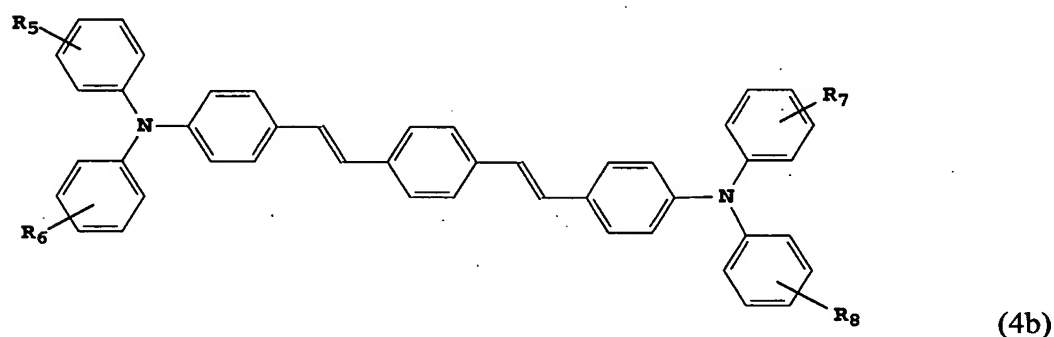
Among derivatives of distyrylarenes that provide blue luminescence, particularly useful are those substituted with diarylamino groups, also known as

distyrylamines. Examples include the general structure 4a and 4b listed below,

5 wherein  $R_1 - R_8$  can be the same or different, and individually represent hydrogen or one or more substituents. For example, substituents can be alkyl groups, such as methyl groups, or aryl groups, such as phenyl groups.

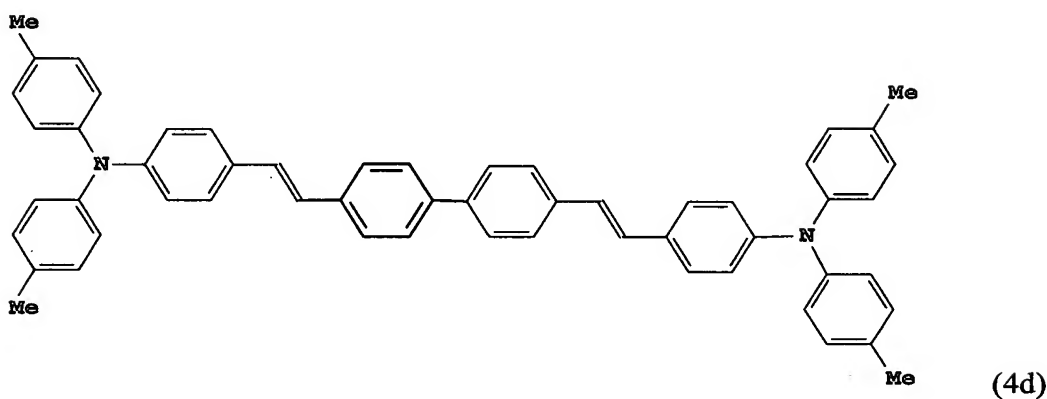
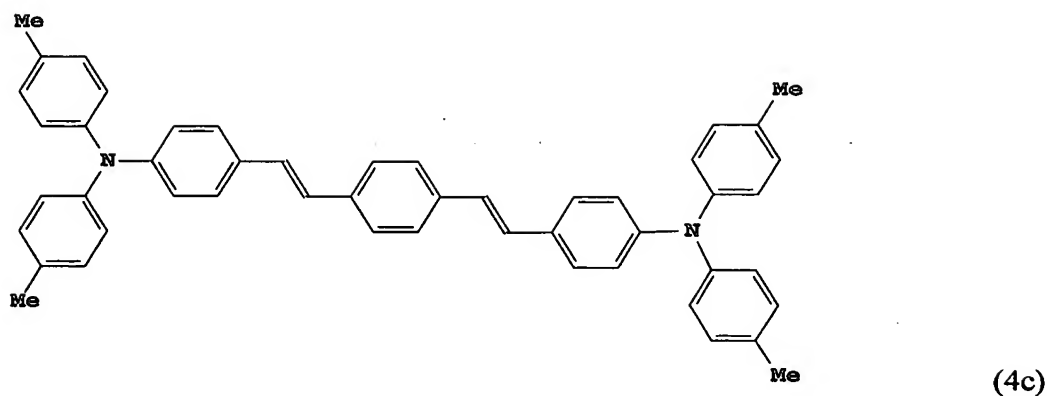


10

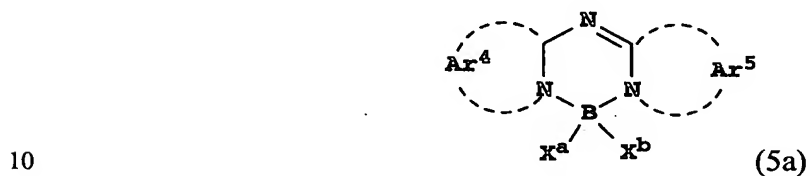


Illustrative examples of useful distyrylamines are blue emitters, 4c and 4d, listed below.

15

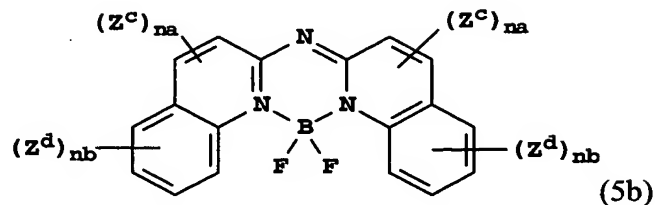


5 Another useful class of blue emitters comprises a boron atom bonded to two nitrogen atoms. Such materials are described in US20030198829A1 and US20030201415A. Suitable blue light-emitting materials are represented by Formula 5a.



10 In Formula 5a, Ar<sup>4</sup> and Ar<sup>5</sup> independently represent the atoms necessary to form a five or six-membered aromatic ring group, such as a pyridine group. X<sup>a</sup> and X<sup>b</sup> represent independently selected substituents, such as fluoro  
15 substituents.

In one desirable embodiment, useful emitting materials that contain boron are described by Formula 5b.

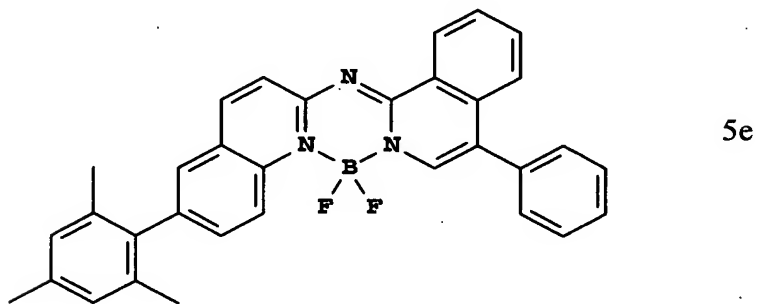
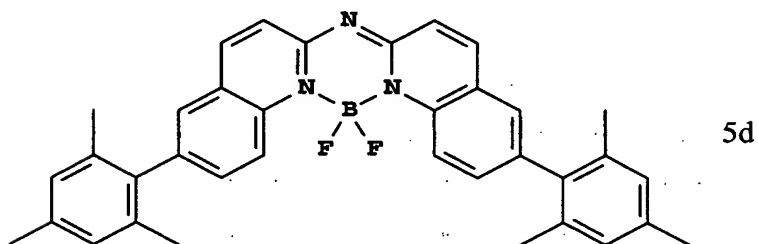
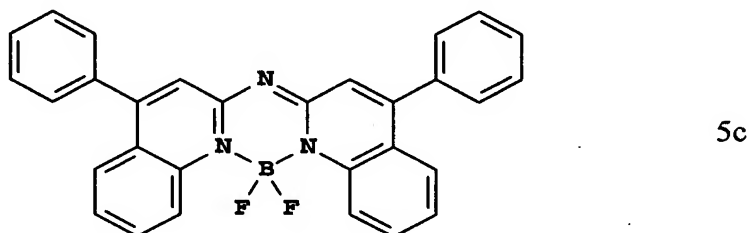


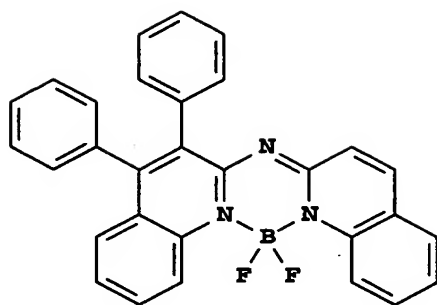
5

In Formula 5b,  $Z^c$  and  $Z^d$  independently represent hydrogen or an independently selected substituent, such as a phenyl group or mesityl group,  $na$  independently represents 0, 1, or 2,  $nb$  independently represents 0-4.

Examples of useful blue emitters that comprise a boron atom bonded to two nitrogen atoms are shown below.

10



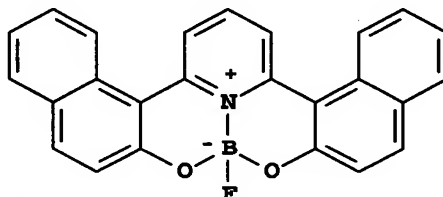


5f

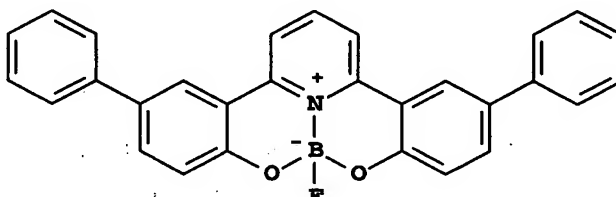
Useful bis(aryloxy)azine borohalide complexes of the invention can be synthesized by methods known in the literature. Desirably a suitable ligand is prepared and the ligand is then complexed to boron. For an example of the  
 5 preparation of suitable boron complexes see Y. Li, Y Liu, W. Bu, J. Guo and Y. Wang, *Chem. Comm. (Cambridge)* **16**, 1551, (2000).

Illustrative examples of bis(aryloxy)azine borohalide complexes useful in the present invention include the following compounds.

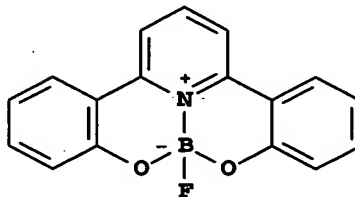
Inv-1



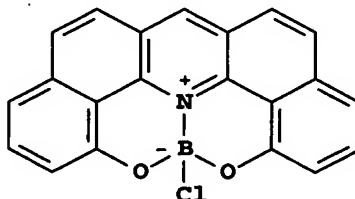
Inv-2



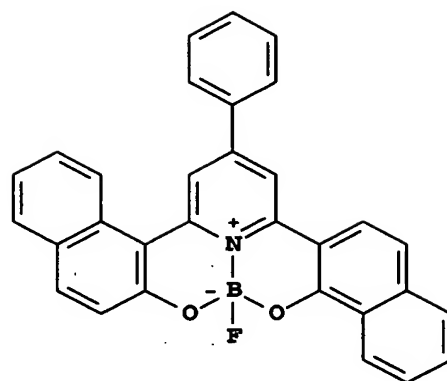
Inv-3



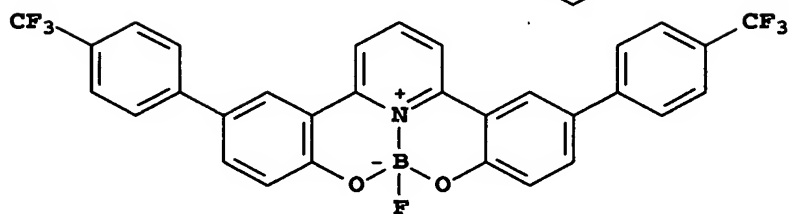
Inv-4



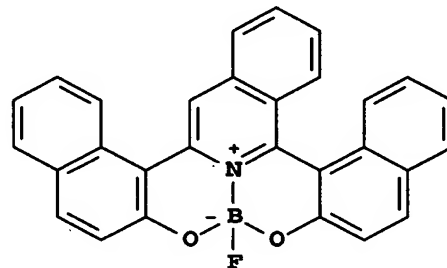
Inv-5



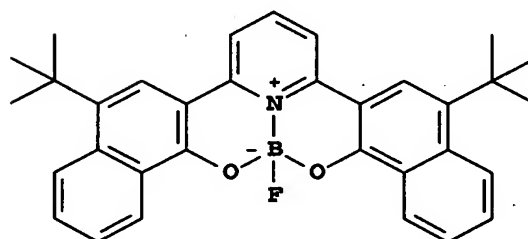
Inv-6



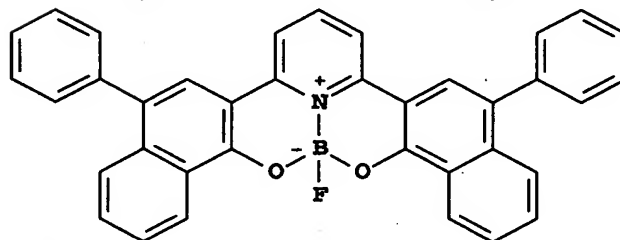
Inv-7



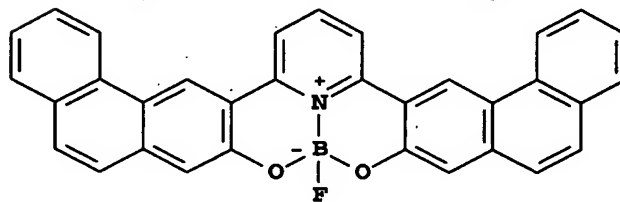
Inv-8



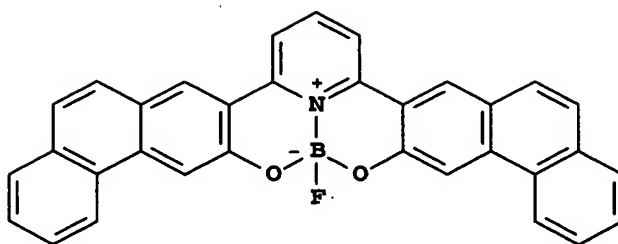
Inv-9



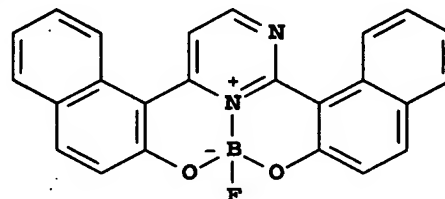
Inv-10



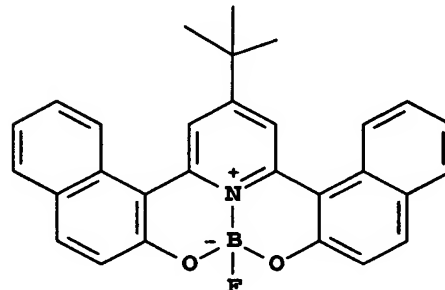
Inv-11



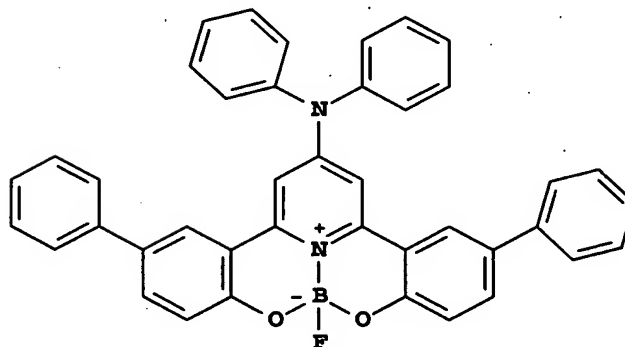
Inv-12



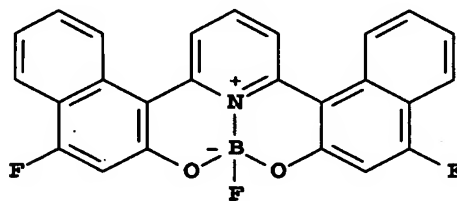
Inv-13



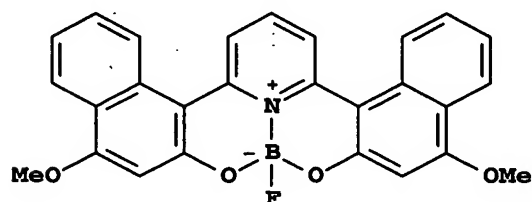
Inv-14



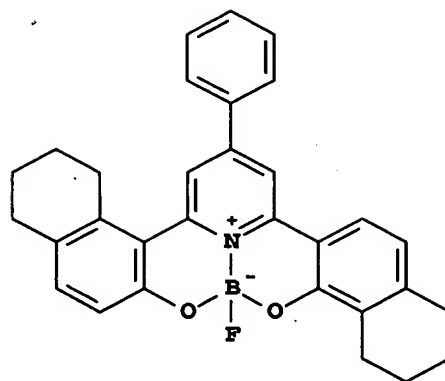
Inv-15



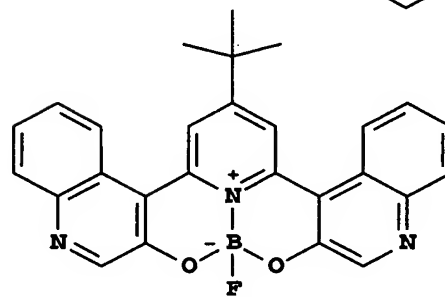
Inv-16



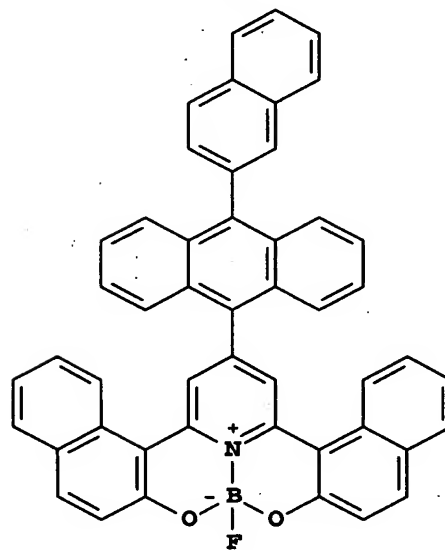
Inv-17



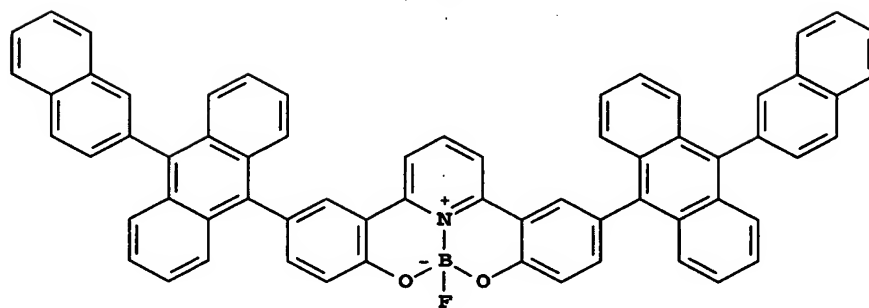
Inv-18



Inv-19



Inv-20



Embodiments of the invention provide not only good luminance efficiency but also a desirable blue or blue-green hue as evidenced by the location and shape of the emission curve of the emitted light. Embodiments of the invention provide materials that sublime readily.

5 Unless otherwise specifically stated, use of the term "substituted" or "substituent" means any group or atom other than hydrogen. Additionally, when the term "group" is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any substituent group  
10 or groups as herein mentioned, so long as the substituent does not destroy properties necessary for device utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl;  
15 cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy,  
20 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, *alpha*-(2,4-di-*t*-pentylphenoxy)acetamido, *alpha*-(2,4-di-*t*-pentylphenoxy)butyramido, *alpha*-(3-pentadecylphenoxy)-hexanamido, *alpha*-(4-hydroxy-3-*t*-butylphenoxy)-  
25 tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, *N*-methyltetradecanamido, *N*-succinimido, *N*-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and *N*-acetyl-*N*-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino,  
30 hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxy carbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecyl-



phenylcarbonylamino, *p*-tolylcarbonylamino, *N*-methylureido, *N,N*-dimethylureido, *N*-methyl-*N*-dodecylureido, *N*-hexadecylureido, *N,N*-dioctadecylureido, *N,N*-dioctyl-*N'*-ethylureido, *N*-phenylureido, *N,N*-diphenylureido, *N*-phenyl-*N*-*p*-tolylureido, *N*-(*m*-hexadecylphenyl)ureido, *N,N*-  
 5 (2,5-di-*t*-pentylphenyl)-*N'*-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-tolylsulfonamido, *p*-dodecylbenzenesulfonamido, *N*-methyltetradecylsulfonamido, *N,N*-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as *N*-methylsulfamoyl, *N*-ethylsulfamoyl, *N,N*-dipropylsulfamoyl, *N*-  
 10 hexadecylsulfamoyl, *N,N*-dimethylsulfamoyl, *N*-[3-(dodecyloxy)propyl]sulfamoyl, *N*-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, *N*-methyl-*N*-tetradecylsulfamoyl, and *N*-dodecylsulfamoyl; carbamoyl, such as *N*-methylcarbamoyl, *N,N*-dibutylcarbamoyl, *N*-octadecylcarbamoyl, *N*-[4-(2,4-di-*t*-  
 15 pentylphenoxy)butyl]carbamoyl, *N*-methyl-*N*-tetradecylcarbamoyl, and *N,N*-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-  
 20 ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl,  
 25 hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-tolylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, *N*-phenylcarbamoyloxy, *N*-ethylcarbamoyloxy, and  
 30 cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (*N*-phenylimido)ethyl, *N*-

succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring  
5 composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen, sulfur, phosphorous, or boron. such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

10 If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired desirable properties for a specific application and can include, for example, electron-withdrawing groups, electron-donating groups, and steric groups. When  
15 a molecule may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents  
20 selected.

#### General Device Architecture

The present invention can be employed in many EL device configurations using small molecule materials, oligomeric materials, polymeric materials, or combinations thereof. These include very simple structures  
25 comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of orthogonal arrays of anodes and cathodes to form pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs).

There are numerous configurations of the organic layers wherein  
30 the present invention can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located

between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure according to the present invention and especially useful for a small molecule device, is shown in FIG. 1 and is comprised of a substrate 101, an anode 103, a hole-injecting layer 105, a hole-transporting layer 107, a light-emitting layer 109, an electron-transporting layer 111, and a cathode 113. These layers are described in detail below. Note that the substrate 101 may alternatively be located adjacent to the cathode 113, or the substrate 101 may actually constitute the anode 103 or cathode 113. The organic layers between the anode 103 and cathode 113 are conveniently referred to as the organic EL element. Also, the total combined thickness of the organic layers is desirably less than 500 nm. If the device includes phosphorescent material, a hole-blocking layer, located between the light-emitting layer and the electron-transporting layer, may be present.

The anode 103 and cathode 113 of the OLED are connected to a voltage/current source through electrical conductors. The OLED is operated by applying a potential between the anode 103 and cathode 113 such that the anode 103 is at a more positive potential than the cathode 113. Holes are injected into the organic EL element from the anode 103 and electrons are injected into the organic EL element at the cathode 113. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time period in the AC cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in US 5,552,678.

#### Substrate

The OLED device of this invention is typically provided over a supporting substrate 101 where either the cathode 113 or anode 103 can be in contact with the substrate. The electrode in contact with the substrate 101 is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode 103, but this invention is not limited to that configuration. The substrate 101 can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable

for viewing the EL emission through the substrate **101**. Transparent glass or plastic is commonly employed in such cases. The substrate **101** can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is  
5 still necessary that the substrate **101**, at least in the emissive pixelated areas, be comprised of largely transparent materials such as glass or polymers. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore the substrate can be light transmissive, light absorbing or light reflective. Substrates  
10 for use in this case include, but are not limited to, glass, plastic, semiconductor materials such as silicon, ceramics, and circuit board materials. Again, the substrate **101** can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

15 Anode

When the desired electroluminescent light emission (EL) is viewed through the anode, the anode **103** should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin  
20 oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode **103**. For applications where EL emission is viewed only through  
25 the cathode **113**, the transmissive characteristics of the anode **103** are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired  
30 anode materials are commonly deposited by any suitable means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means.

Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize short circuits or enhance reflectivity.

#### Cathode

5           When light emission is viewed solely through the anode 103, the cathode 113 used in this invention can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often contain a low  
10   work function metal ( $< 4.0$  eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20 %, as described in U.S. Patent No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising the cathode and a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting  
15   layer (ETL)), the cathode being capped with a thicker layer of a conductive metal. Here, the EIL preferably includes a low work function metal or metal salt, and if so, the thicker capping layer does not need to have a low work function. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent No. 5,677,572. An ETL material doped with an alkali  
20   metal, for example, Li-doped Alq, is another example of a useful EIL. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Patent Nos. 5,059,861, 5,059,862, and 6,140,763.

          When light emission is viewed through the cathode, the cathode  
25   113 must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in US 4,885,211, US 5,247,190, JP 3,234,963, US 5,703,436, US 5,608,287, US 5,837,391, US 5,677,572, US 5,776,622, US 5,776,623, US 5,714,838, US 5,969,474, US 5,739,545, US 5,981,306, US 6,137,223, US 6,140,763, US  
30   6,172,459, EP 1 076 368, US 6,278,236, and US 6,284,3936. Cathode materials are typically deposited by any suitable method such as evaporation, sputtering, or

chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in US 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

5     Hole-Injecting Layer (HIL)

A hole-injecting layer 105 may be provided between anode 103 and hole-transporting layer 107. The hole-injecting layer can serve to improve the film formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer 107. Suitable materials for use in the hole-injecting layer 105 include, but are not limited to, porphyrinic compounds as described in US 4,720,432, plasma-deposited fluorocarbon polymers as described in US 6,208,075, and some aromatic amines, for example, MTDATA (4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine). Alternative hole-injecting materials reportedly useful in organic EL devices are described in

10     EP 0 891 121 A1 and EP 1 029 909 A1. A hole-injection layer is conveniently used in the present invention, and is desirably a plasma-deposited fluorocarbon polymer. The thickness of a hole-injection layer containing a plasma-deposited fluorocarbon polymer can be in the range of 0.2 nm to 15 nm and suitably in the range of 0.3 to 1.5 nm.

20     Hole-Transporting Layer (HTL)

While not always necessary, it is often useful to include a hole-transporting layer in an OLED device. The hole-transporting layer 107 of the organic EL device contains at least one hole-transporting compound such as an aromatic tertiary amine, where the latter is understood to be a compound

25     containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylaminers are illustrated by Klupfel et al. US 3,180,730. Other suitable triarylaminers substituted

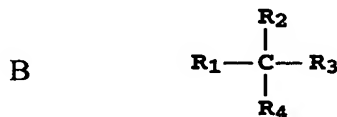
30     with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al US 3,567,450 and US 3,658,520.

A more preferred class of aromatic tertiary amines is those which include at least two aromatic tertiary amine moieties as described in US 4,720,432 and US 5,061,569. Such compounds include those represented by structural formula (A).



5 wherein Q<sub>1</sub> and Q<sub>2</sub> are independently selected aromatic tertiary amine moieties and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond. In one embodiment, at least one of Q<sub>1</sub> or Q<sub>2</sub> contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is  
 10 conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural formula (A) and containing two triarylamine moieties is represented by structural formula (B):



where

R<sub>1</sub> and R<sub>2</sub> each independently represents a hydrogen atom, an aryl group,  
 15 or an alkyl group or R<sub>1</sub> and R<sub>2</sub> together represent the atoms completing a cycloalkyl group; and

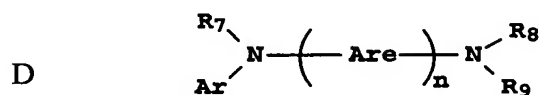
R<sub>3</sub> and R<sub>4</sub> each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (C):



20 wherein R<sub>5</sub> and R<sub>6</sub> are independently selected aryl groups. In one embodiment, at least one of R<sub>5</sub> or R<sub>6</sub> contains a polycyclic fused ring structure, e.g., a naphthalene.

Another class of aromatic tertiary amines is the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by

formula (C), linked through an arylene group. Useful tetraaryldiamines include those represented by formula (D).



wherein

each Are is an independently selected arylene group, such as a phenylene  
5 or anthracene moiety,

n is an integer of from 1 to 4, and

Ar, R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> is a polycyclic fused ring structure, e.g., a naphthalene.

10 The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (A), (B), (C), (D), can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halide such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The  
15 cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

The hole-transporting layer can be formed of a single tertiary amine  
20 compound or a mixture of such compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (B), in combination with a tetraaryldiamine, such as indicated by formula (D). Illustrative of useful aromatic tertiary amines are the following:

1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC)  
25 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-methylcyclohexane  
1,1-Bis(4-di-*p*-tolylaminophenyl)-4-phenylcyclohexane  
1,1-Bis(4-di-*p*-tolylaminophenyl)-3-phenylpropane (TAPPP)  
*N,N,N',N'*-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl  
Bis(4-dimethylamino-2-methylphenyl)phenylmethane



- 1,4-bis[2-[4-[*N,N*-di(*p*-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB)  
*N,N,N',N'*-Tetra-*p*-tolyl-4,4'-diaminobiphenyl (TTB)  
*N,N,N',N'*-Tetraphenyl-4,4'-diaminobiphenyl  
*N,N,N',N'*-tetra-1-naphthyl-4,4'-diaminobiphenyl  
5 *N,N,N',N'*-tetra-2-naphthyl-4,4'-diaminobiphenyl  
*N*-Phenylcarbazole  
4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB)  
4,4'-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB)  
4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]*p*-terphenyl  
10 4,4'-Bis[*N*-(2-naphthyl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(3-acenaphthenyl)-*N*-phenylamino]biphenyl  
1,5-Bis[*N*-(1-naphthyl)-*N*-phenylamino]naphthalene  
4,4'-Bis[*N*-(9-anthryl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(1-anthryl)-*N*-phenylamino]-*p*-terphenyl  
15 4,4'-Bis[*N*-(2-phenanthryl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(8-fluoranthryl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(2-pyrenyl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(2-naphthacenyl)-*N*-phenylamino]biphenyl  
4,4'-Bis[*N*-(2-perylenyl)-*N*-phenylamino]biphenyl  
20 4,4'-Bis[*N*-(1-coronenyl)-*N*-phenylamino]biphenyl  
2,6-Bis(di-*p*-tolylamino)naphthalene  
2,6-Bis[di-(1-naphthyl)amino]naphthalene  
2,6-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]naphthalene  
*N,N,N',N'*-Tetra(2-naphthyl)-4,4''-diamino-*p*-terphenyl  
25 4,4'-Bis{*N*-phenyl-*N*-[4-(1-naphthyl)-phenyl]amino}biphenyl  
2,6-Bis[*N,N*-di(2-naphthyl)amino]fluorene  
4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA)  
4,4'-Bis[*N*-(3-methylphenyl)-*N*-phenylamino]biphenyl (TPD)

Another class of useful hole-transporting materials includes  
30 polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups may be used including oligomeric

materials. In addition, polymeric hole-transporting materials can be used such as poly(*N*-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene) / poly(4-styrenesulfonate) also called PEDOT/PSS. It is also possible for the hole-transporting layer to  
5 comprise two or more sublayers of differing compositions, the composition of each sublayer being as described above. The thickness of the hole-transporting layer can be between 10 and about 500 nm and suitably between 50 and 300 nm.

#### Light-Emitting Layer (LEL)

In addition to the light-emitting materials of this invention,  
10 additional light emitting materials may be used in the EL device, including other fluorescent materials. Other fluorescent materials may be used in the same layer as the boron complex material, in adjacent layers, in adjacent pixels, or any combination.

As more fully described in U.S. Patent Nos. 4,769,292 and  
15 5,935,721, the light-emitting layer (LEL) of the organic EL element includes a luminescent material where electroluminescence is produced as a result of electron-hole pair recombination. The light-emitting layer can be comprised of a single material, but more commonly consists of a host material doped with a guest emitting material or materials where light emission comes primarily from the  
20 emitting materials and can be of any color. The host materials in the light-emitting layer can be an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material or combination of materials that support hole-electron recombination. Fluorescent emitting materials are typically incorporated at 0.01 to 10 % by weight of the host material.

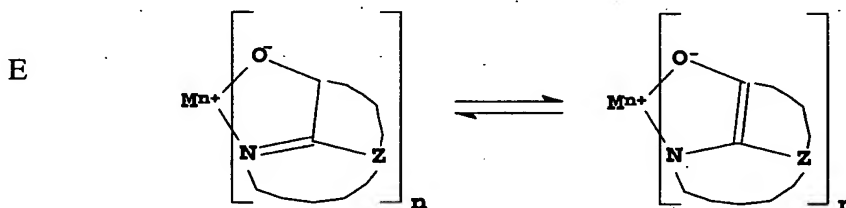
25 The host and emitting materials can be small non-polymeric molecules or polymeric materials such as polyfluorenes and polyvinylarylenes (e.g., poly(*p*-phenylenevinylene), PPV). In the case of polymers, small-molecule emitting materials can be molecularly dispersed into a polymeric host, or the emitting materials can be added by copolymerizing a minor constituent into a host  
30 polymer. Host materials may be mixed together in order to improve film formation, electrical properties, light emission efficiency, operating lifetime, or

manufacturability. The host may comprise a material that has good hole-transporting properties and a material that has good electron-transporting properties.

An important relationship for choosing a fluorescent material as a guest emitting material is a comparison of the excited singlet-state energies of the host and the fluorescent material. It is highly desirable that the excited singlet-state energy of the fluorescent material be lower than that of the host material. The excited singlet-state energy is defined as the difference in energy between the emitting singlet state and the ground state. For non-emissive hosts, the lowest excited state of the same electronic spin as the ground state is considered the emitting state.

Host and emitting materials known to be of use include, but are not limited to, those disclosed in US 4,768,292, US 5,141,671, US 5,150,006, US 5,151,629, US 5,405,709, US 5,484,922, US 5,593,788, US 5,645,948, US 5,683,823, US 5,755,999, US 5,928,802, US 5,935,720, US 5,935,721, and US 6,020,078.

Metal complexes of 8-hydroxyquinoline and similar derivatives, also known as metal-chelated oxinoid compounds (Formula E), constitute one class of useful host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.



wherein

M represents a metal;

n is an integer of from 1 to 4; and

Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; a trivalent metal, such aluminum or gallium, or another metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or tetravalent metal known to be a useful chelating metal can be employed.

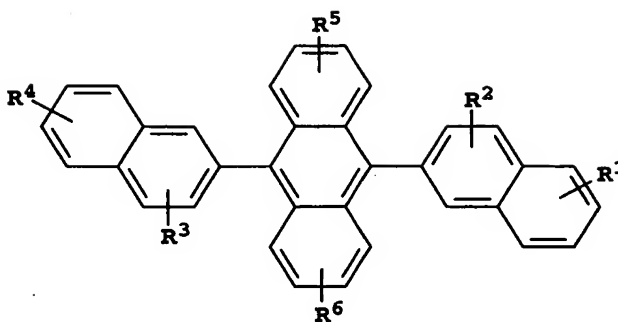
Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function the number of ring atoms is usually maintained at 18 or less.

Illustrative of useful chelated oxinoid compounds are the following:

- CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]
- CO-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]
- CO-3: Bis[benzo{f}-8-quinolinolato]zinc (II)
- CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)- $\mu$ -oxo-bis(2-methyl-8-quinolinolato) aluminum(III)
- CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]
- CO-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato)aluminum(III)]
- CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]
- CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]
- CO-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

As already mentioned, derivatives of 9,10-di-(2-naphthyl)anthracene (Formula F) constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.

F



wherein:  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  represent one or more substituents on each ring where each substituent is individually selected from the following groups:

Group 1: hydrogen, or alkyl of from 1 to 24 carbon atoms;

5 Group 2: aryl or substituted aryl of from 5 to 20 carbon atoms;

Group 3: carbon atoms from 4 to 24 necessary to complete a fused aromatic ring of anthracenyl; pyrenyl, or perylenyl;

Group 4: heteroaryl or substituted heteroaryl of from 5 to 24 carbon atoms as necessary to complete a fused heteroaromatic ring of furyl, thienyl, pyridyl,  
10 quinoliny or other heterocyclic systems;

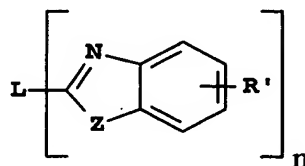
Group 5: alkoxyamino, alkylamino, or arylamino of from 1 to 24 carbon atoms; and

Group 6: fluorine, chlorine, bromine or cyano.

Illustrative examples include 9,10-di-(2-naphthyl)anthracene and 2-  
15 *t*-butyl-9,10-di-(2-naphthyl)anthracene. Other anthracene derivatives can be useful as a host in the LEL, including derivatives of 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene.

Benzazole derivatives (Formula G) constitute another class of useful host materials capable of supporting electroluminescence, and are  
20 particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.

G



wherein:

n is an integer of 3 to 8;

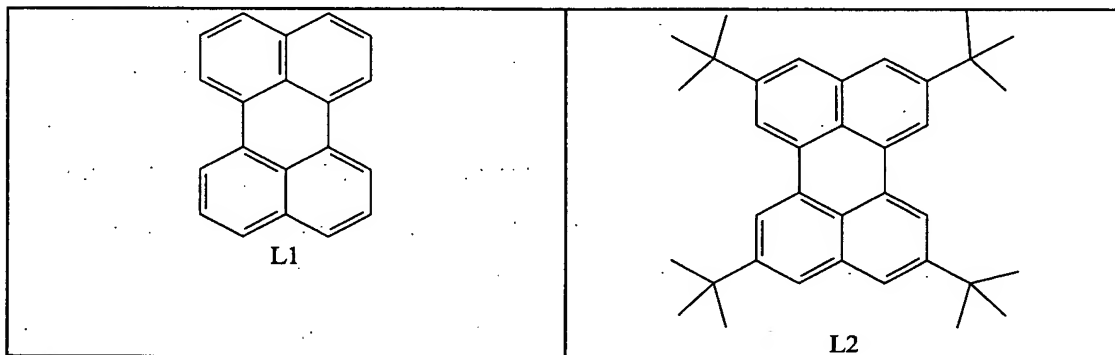
Z is O, NR or S; and

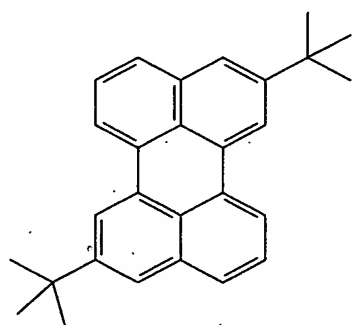
R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms,  
5 for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted  
aryl of from 5 to 20 carbon atoms for example phenyl and naphthyl, furyl, thienyl,  
pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro;  
or atoms necessary to complete a fused aromatic ring; and

L is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted  
10 aryl, which connects the multiple benzazoles together. L may be either conjugated  
with the multiple benzazoles or not in conjugation with them. An example of a  
useful benzazole is 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

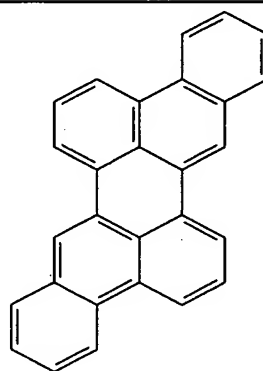
Styrylarylene derivatives as described in U.S. Patent 5,121,029 and JP  
08333569 are also useful hosts for blue emission. For example, 9,10-bis[4-(2,2-  
15 diphenylethenyl)phenyl]anthracene and 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl  
(DPVBi) are useful hosts for blue emission.

Useful fluorescent emitting materials include, but are not limited  
to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin,  
rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran  
20 compounds, polymethine compounds, pyrylium and thiapyrylium compounds,  
fluorene derivatives, perflanthene derivatives, indenoperylene derivatives,  
bis(azinyl)amine boron compounds, bis(azinyl)methane compounds, and  
carbostyryl compounds. Illustrative examples of useful materials include, but are  
not limited to, the following:

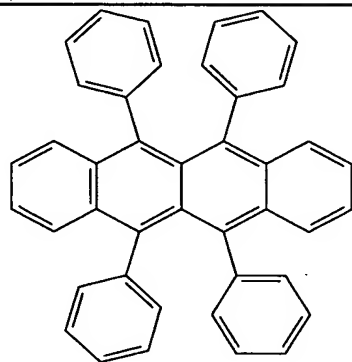




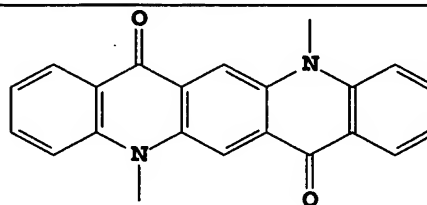
L3



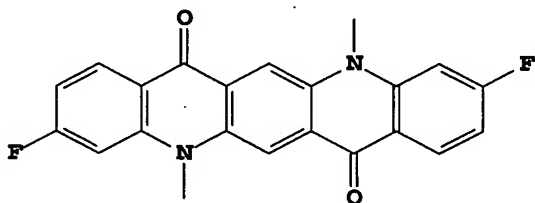
L4



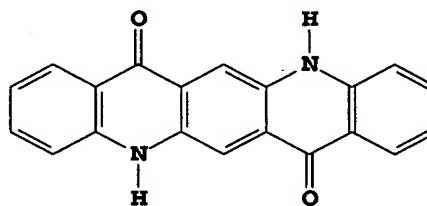
L5



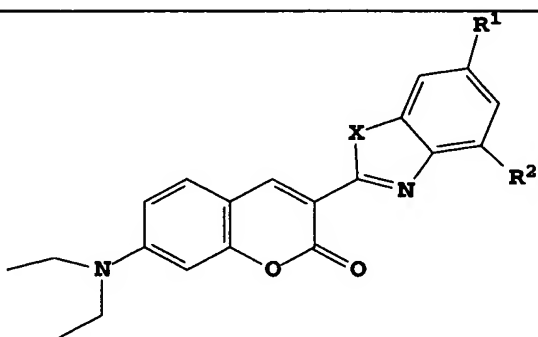
L6



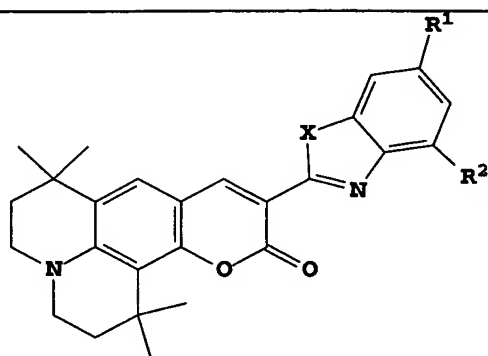
L7



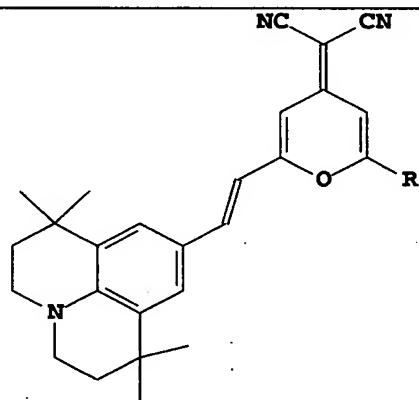
L8



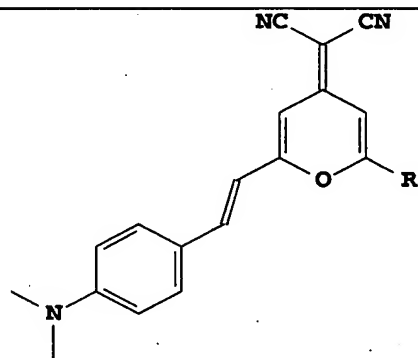
	<u>X</u>	<u>R1</u>	<u>R2</u>
L9	O	H	H
L10	O	H	Methyl
L11	O	Methyl	H
L12	O	Methyl	Methyl
L13	O	H	<i>t</i> -butyl
L14	O	<i>t</i> -butyl	H
L15	O	<i>t</i> -butyl	<i>t</i> -butyl
L16	S	H	H
L17	S	H	Methyl
L18	S	Methyl	H
L19	S	Methyl	Methyl
L20	S	H	<i>t</i> -butyl
L21	S	<i>t</i> -butyl	H
L22	S	<i>t</i> -butyl	<i>t</i> -butyl



	<u>X</u>	<u>R1</u>	<u>R2</u>
L23	O	H	H
L24	O	H	Methyl
L25	O	Methyl	H
L26	O	Methyl	Methyl
L27	O	H	<i>t</i> -butyl
L28	O	<i>t</i> -butyl	H
L29	O	<i>t</i> -butyl	<i>t</i> -butyl
L30	S	H	H
L31	S	H	Methyl
L32	S	Methyl	H
L33	S	Methyl	Methyl
L34	S	H	<i>t</i> -butyl
L35	S	<i>t</i> -butyl	H
L36	S	<i>t</i> -butyl	<i>t</i> -butyl

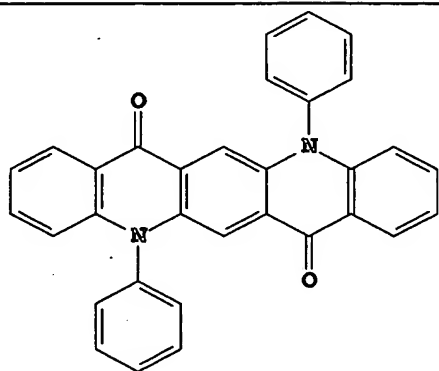


	<u>R</u>
L37	phenyl
L38	methyl
L39	<i>t</i> -butyl
L40	mesityl

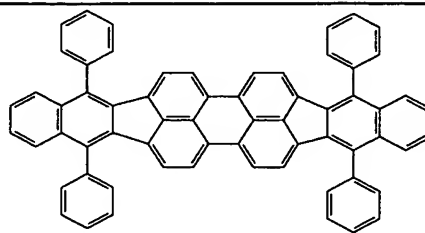


	<u>R</u>
L41	phenyl
L42	methyl
L43	<i>t</i> -butyl
L44	mesityl

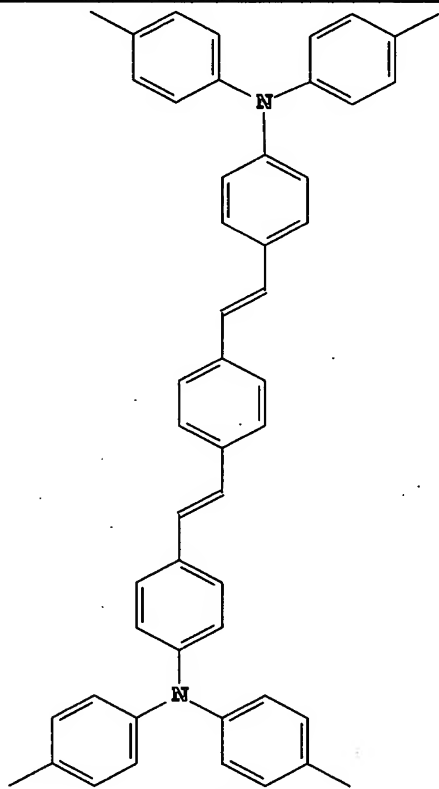




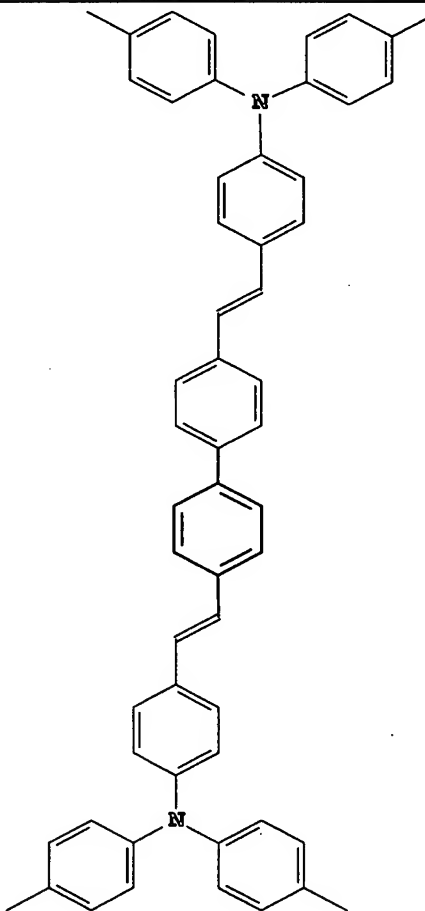
L45



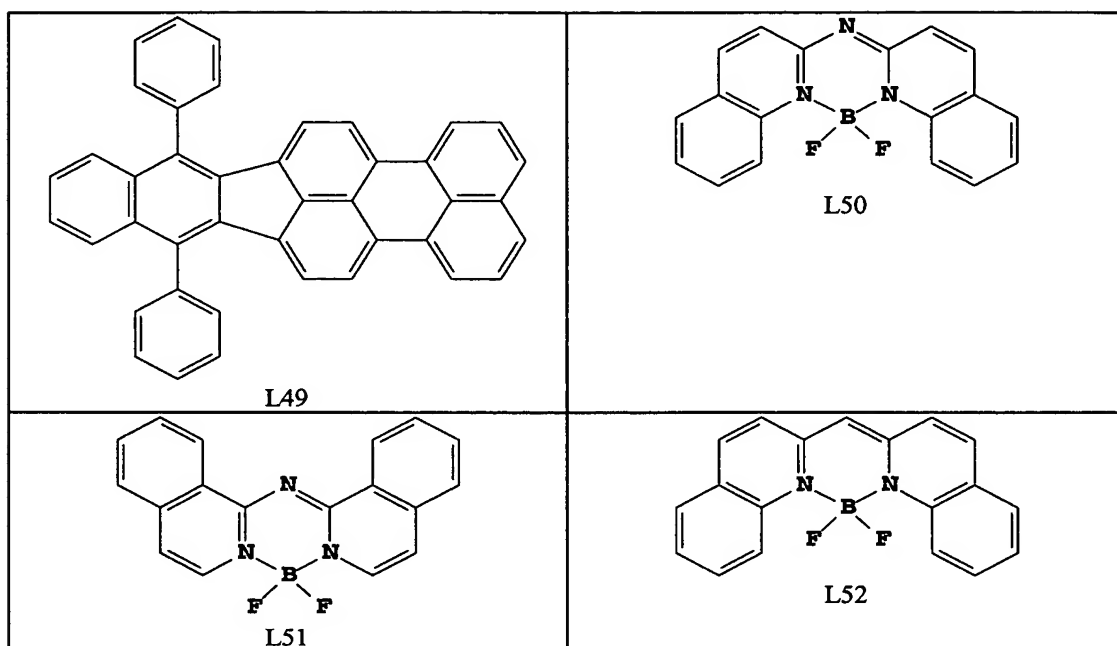
L46



L47



L48



In addition to the light-emitting materials of this invention, light-emitting phosphorescent materials may be used in the EL device. For convenience, the phosphorescent complex guest material may be referred to herein as a phosphorescent material. The phosphorescent material typically includes one or more ligands, for example monoanionic ligands that can be coordinated to a metal through an  $sp^2$  carbon and a heteroatom. Conveniently, the ligand can be phenylpyridine (ppy) or derivatives or analogs thereof. Examples of some useful phosphorescent organometallic materials include tris(2-phenylpyridinato- $N,C^2'$ )iridium(III), bis(2-phenylpyridinato- $N,C^2'$ )iridium(III)(acetylacetonate), and bis(2-phenylpyridinato- $N,C^2'$ )platinum(II). Usefully, many phosphorescent organometallic materials emit in the green region of the spectrum, that is, with a maximum emission in the range of 510 to 570 nm.

Phosphorescent materials may be used singly or in combinations other phosphorescent materials, either in the same or different layers. Phosphorescent materials and suitable hosts are described in WO 00/57676, WO 00/70655, WO 01/41512 A1; WO 02/15645 A1, US 2003/0017361 A1, WO 01/93642 A1, WO 01/39234 A2, US 6,458,475 B1, WO 02/071813 A1, US 6,573,651 B2, US 2002/0197511 A1, WO 02/074015 A2, US 6,451,455 B1, US

2003/ 0072964 A1, US 2003 / 0068528 A1, US 6,413,656 B1, US 6,515,298 B2,  
US 6,451,415 B1, US 6,097,147, US 2003/0124381 A1, US 2003/0059646 A1,  
US 2003/0054198 A1, EP 1 239 526 A2, EP 1 238 981 A2, EP 1 244 155 A2, US  
2002/0100906 A1, US 2003 / 0068526 A1, US 2003/0068535 A1, JP  
5 2003073387A, JP 2003 073388A, US 2003/0141809 A1, US 2003/0040627 A1,  
JP 2003059667A, JP 2003073665A, and US 2002/0121638 A1.

The emission wavelengths of cyclometallated Ir(III) complexes of  
the type  $\text{IrL}_3$  and  $\text{IrL}_2\text{L}'$ , such as the green-emitting *fac*-tris(2-phenylpyridinato-  
 $N, C^{2'}$ )iridium(III) and bis(2-phenylpyridinato- $N, C^{2'}$ )iridium(III)(acetylacetonate)  
10 may be shifted by substitution of electron donating or withdrawing groups at  
appropriate positions on the cyclometallating ligand L, or by choice of different  
heterocycles for the cyclometallating ligand L. The emission wavelengths may  
also be shifted by choice of the ancillary ligand L'. Examples of red emitters are  
the bis(2-(2'-benzothienyl)pyridinato- $N, C^{3'}$ )iridium(III)(acetylacetonate) and  
15 tris(2-phenylisoquinolino- $N, C$ )iridium(III). A blue-emitting example is bis(2-  
(4,6-difluorophenyl)-pyridinato- $N, C^{2'}$ )iridium(III)(picolinate).

Red electrophosphorescence has been reported, using bis(2-(2'-  
benzo[4,5-a]thienyl)pyridinato- $N, C^3$ ) iridium (acetylacetonate) [ $\text{Btp}_2\text{Ir}(\text{acac})$ ] as  
the phosphorescent material (C. Adachi, S. Lamansky, M. A. Baldo, R. C. Kwong,  
20 M. E. Thompson, and S. R. Forrest, *App. Phys. Lett.*, **78**, 1622-1624 (2001)).

Other important phosphorescent materials include cyclometallated  
Pt(II) complexes such as cis-bis(2-phenylpyridinato- $N, C^{2'}$ )platinum(II), cis-bis(2-  
(2'-thienyl)pyridinato- $N, C^{3'}$ ) platinum(II), cis-bis(2-(2'-thienyl)quinolino- $N, C^{5'}$ )  
platinum(II), or (2-(4,6-difluorophenyl)pyridinato- $N, C^{2'}$ ) platinum (II)  
25 (acetylacetonate). Pt (II) porphyrin complexes such as 2,3,7,8,12,13,17,18-  
octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent  
materials.

Still other examples of useful phosphorescent materials include  
coordination complexes of the trivalent lanthanides such as  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  (J. Kido  
30 et al., *Appl. Phys. Lett.*, **65**, 2124 (1994)).

Suitable host materials for phosphorescent materials should be selected so that transfer of a triplet exciton can occur efficiently from the host material to the phosphorescent material but cannot occur efficiently from the phosphorescent material to the host material. Therefore, it is highly desirable that the triplet energy of the phosphorescent material be lower than the triplet energy of the host. Generally speaking, a large triplet energy implies a large optical bandgap. However, the band gap of the host should not be chosen so large as to cause an unacceptable barrier to injection of charge carriers into the light-emitting layer and an unacceptable increase in the drive voltage of the OLED. Suitable host materials are described in WO 00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, and US 20020117662. Suitable hosts include certain aryl amines, triazoles, indoles and carbazole compounds. Examples of desirable hosts are 4,4'-*N,N'*-dicarbazole-biphenyl, otherwise known as 4,4'-bis(carbazol-9-yl)biphenyl or CBP; 4,4'-*N,N'*-dicarbazole-2,2'-dimethyl-biphenyl, otherwise known as 2,2'-dimethyl-4,4'-bis(carbazol-9-yl)biphenyl or CDBP; 1,3-bis(*N,N'*-dicarbazole)benzene, otherwise known as 1,3-bis(carbazol-9-yl)benzene, and poly(*N*-vinylcarbazole), including their derivatives.

Desirable host materials are capable of forming a continuous film.

#### Hole-Blocking Layer (HBL)

In addition to suitable hosts, an OLED device employing a phosphorescent material often requires at least one hole-blocking layer placed between the electron-transporting layer 111 and the light-emitting layer 109 to help confine the excitons and recombination events to the light-emitting layer comprising the host and phosphorescent material. In this case, there should be an energy barrier for hole migration from the host into the hole-blocking layer, while electrons should pass readily from the hole-blocking layer into the light-emitting layer comprising a host and a phosphorescent material. The first requirement entails that the ionization potential of the hole-blocking layer be larger than that of the light-emitting layer 109, desirably by 0.2 eV or more. The second requirement entails that the electron affinity of the hole-blocking layer not greatly exceed that of the light-emitting layer 109, and desirably be either less than that of light-

emitting layer or not exceed that of the light-emitting layer by more than about 0.2 eV.

When used with an electron-transporting layer whose characteristic luminescence is green, such as an Alq-containing electron-transporting layer as described below, the requirements concerning the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the material of the hole-blocking layer frequently result in a characteristic luminescence of the hole-blocking layer at shorter wavelengths than that of the electron-transporting layer, such as blue, violet, or ultraviolet luminescence. Thus, it is desirable that the characteristic luminescence of the material of a hole-blocking layer be blue, violet, or ultraviolet. It is further desirable, but not absolutely required, that the triplet energy of the hole-blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2 and WO 01/93642 A1. Two examples of useful hole-blocking materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum(III) (BALq). The characteristic luminescence of BCP is in the ultraviolet, and that of BALq is blue. Metal complexes other than BALq are also known to block holes and excitons as described in US 20030068528. In addition, US 20030175553 A1 describes the use of *fac*-tris(1-phenylpyrazolato-*N,C*<sup>2'</sup>)iridium(III) (Irppz) for this purpose.

When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

#### Electron-Transporting Layer (ETL)

Desirable thin film-forming materials for use in forming the electron-transporting layer 111 of the organic EL devices of this invention are metal-chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons, exhibit high levels of performance, and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (E), previously described.

Other electron-transporting materials suitable for use in the electron-transporting layer 111 include various butadiene derivatives as disclosed in US 4,356,429 and various heterocyclic optical brighteners as described in US 4,539,507. Benzazoles satisfying structural formula (G) are also useful electron transporting materials. Triazines are also known to be useful as electron transporting materials.

If both a hole-blocking layer and an electron-transporting layer 111 are used, electrons should pass readily from the electron-transporting layer 111 into the hole-blocking layer. Therefore, the electron affinity of the electron-transporting layer 111 should not greatly exceed that of the hole-blocking layer. Desirably, the electron affinity of the electron-transporting layer should be less than that of the hole-blocking layer or not exceed it by more than about 0.2 eV.

If an electron-transporting layer is used, its thickness may be between 2 and 100 nm and suitably between 5 and 20 nm.

#### Other Useful Organic Layers and Device Architecture

In some instances, layers 109 through 111 can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. The hole-blocking layer, when present, and layer 111 may also be collapsed into a single layer that functions to block holes or excitons, and supports electron transport. It also known in the art that emitting materials may be included in the hole-transporting layer 107. In that case, the hole-transporting material may serve as a host. Multiple materials may be added to one or more layers in order to create a white-emitting OLED, for example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, US 20020025419, EP 1 182 244, US 5,683,823, US 5,503,910, US 5,405,709, and US 5,283,182 and can be equipped with a suitable filter arrangement to produce a color emission.

This invention may be used in so-called stacked device architecture, for example, as taught in US 5,703,436 and US 6,337,492.

### Deposition of Organic Layers

The organic materials mentioned above are suitably deposited by any means suitable for the form of the organic materials. In the case of small molecules, they are conveniently deposited through sublimation or evaporation, but can be deposited by other means such as coating from a solvent together with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation or evaporation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in US 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (US 5,294,870), spatially-defined thermal dye transfer from a donor sheet (US 5,688,551, US 5,851,709 and US 6,066,357) or an inkjet method (US 6,066,357).

### Encapsulation

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon, along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Patent No. 6,226,890. In addition, barrier layers such as SiO<sub>x</sub>, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation. Any of these methods of sealing or encapsulation and desiccation can be used with the EL devices constructed according to the present invention.

### Optical Optimization

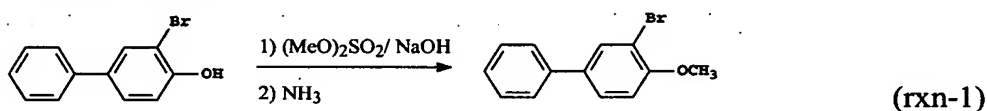
OLED devices of this invention can employ various well-known optical effects in order to enhance their emissive properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing electrodes, providing anti-glare or anti-reflection coatings over the

display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings may be specifically provided over the EL device or as part of the EL device.

5                    Embodiments of the invention may provide advantageous features such as higher luminous yield, lower drive voltage, and higher power efficiency, reduced sublimation temperatures, and simplified manufacture. Embodiments of the compounds useful in the invention may also provide a wide range of hues including those useful in the emission of white light (directly or through filters to  
10 provide multicolor displays). Embodiments of the invention can also provide an area lighting device.

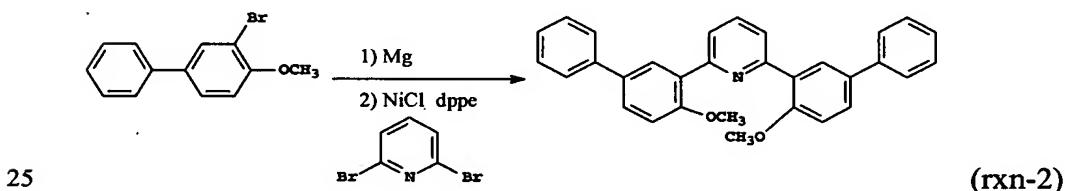
The invention and its advantages can be better appreciated by the following examples.

15    Synthetic Example



Preparation of 3-Bromo-4-methoxy-1,1'-biphenyl (rxn-1)

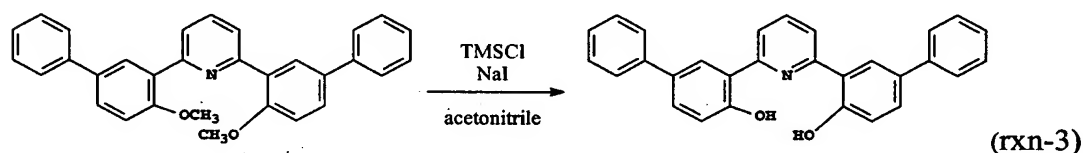
Dimethylsulfate (10.3 mL, 109 mmol) was added to a mixture of 3-  
20 bromo-[1,1'-biphenyl]-4-ol and sodium hydroxide (8 g, 201 mmol) in water (12.4 mL) at 0 °C. After stirring for 2 hours at reflux, ammonia (1.2 mL) was added to the mixture. The solid was filtered and washed with water. The product, 3-bromo-4-methoxy-1,1'-biphenyl, was crystallized from heptane.



Preparation of 2,6-bis((2-methoxy-5-phenyl)phenyl)pyridine (rxn-2)

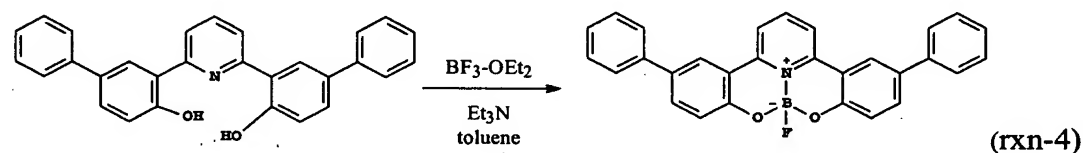


3-Bromo-4-methoxy-1,1'-biphenyl (7 g, 26.6 mmol) was added to a mixture of magnesium (0.97 g, 399 mmol) in THF (80 mL). The mixture was stirred at reflux until the Grignard reagent formed. After the mixture was cooled to 0 °C, it was transferred to a mixture of 2,6-dibromopyridine (3.2 g, 13.3 mmol) and 1,2-bis(diphenylphosphino)ethane nickel chloride (0.7 g, 1.33 mmol) in THF (35 mL). After stirring at room temperature overnight, a saturated solution of ammonium chloride was added. The mixture was extracted with methylene chloride. The organic layers were dried with magnesium sulfate, filtered, and concentrated. The product, 2,6-bis((2-methoxy-5-phenyl)phenyl)pyridine, was purified by recrystallization.



Preparation of 2,6-bis((2-hydroxy-5-phenyl)phenyl)pyridine (rxn-3).

Chlorotrimethylsilane (4.1 mL, 32.5 mmol) and sodium iodide (4.9 g, 32.5 mmol) were added to a solution of the methyl ether (3.6 g, 8.12 mmol) in acetonitrile (16 mL). After stirring overnight, water was added to the mixture. The mixture was extracted with methylene chloride. The organic layers were dried with magnesium sulfate, filtered, and concentrated. The product, 2,6-bis((2-hydroxy-5-phenyl)phenyl)pyridine, was purified by column chromatography.



Preparation of Inv-2 (rxn-4).

BF<sub>3</sub>-OEt<sub>2</sub> (0.52 mL, 4.1 mmol) was added to a mixture of the alcohol, 2,6-bis((2-hydroxy-5-phenyl)phenyl)pyridine, (1.7 g, 4.1 mmol) and triethylamine (0.57 mL, 4.1 mmol) in toluene (14 mL). The mixture was stirred at

reflux overnight. After cooling to room temperature, water was added. The mixture was extracted with methylene chloride. The organic layers were dried with magnesium sulfate, filtered, and concentrated. The product, Inv-2, was purified by column chromatography.

5

#### Device Example 1 – EL Device Fabrication of Samples 1-5

An EL device (Sample 1) satisfying the requirements of the invention was constructed in the following manner:

- 10 1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO) as the anode was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
- 15 2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of  $\text{CHF}_3$ .
- 20 3. A hole-transporting layer (HTL) of *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 75 nm was then evaporated from a tantalum boat.
4. A 20 nm light-emitting layer (LEL) of 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene (TBADN) and Inv-1 (0.50 wt%) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
- 25 5. A 35 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) ( $\text{AlQ}_3$ ) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.
- 30 6. On top of the  $\text{AlQ}_3$  layer was deposited a 220 nm cathode formed of a 10:1 volume ratio of Mg and Ag.

The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

EL devices, Samples 2, 3, and 4, incorporating Inv-1 were fabricated in an identical manner as Sample 1 but Inv-1 was used at the levels indicated in the Table 1. Sample 5 was prepared in the same manner as Sample 1 except Inv-1 was omitted. The cells thus formed were tested for efficiency and color at an operating current of 20 mA/cm<sup>2</sup> and the results are reported in Table 1 in the form of output efficiency (W/A), luminance yield (cd/A), maximum wavelength ( $\lambda_{\max}$ ) of emission and CIE (Commission Internationale de L'Eclairage) coordinates.

Table 1. Evaluation Results for EL devices 1-5.

Sample	Level (%)	Efficiency (W/A)	Yield (cd/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	Emission $\lambda_{\max}$ (nm)	Type
1	0.50	0.033	1.82	0.154	0.182	464	Invention
2	1.00	0.030	1.90	0.156	0.222	464	Invention
3	2.00	0.027	1.92	0.160	0.261	468	Invention
4	4.00	0.025	1.95	0.169	0.297	472	Invention
5	0.00	0.035	1.34	0.159	0.113	444	Comparison

As can be seen from Table 1, all tested EL devices incorporating the invention light-emitting material exhibit blue or blue-green electroluminescence with a desired yield.

#### 20 Device Example 2 – EL Device Fabrication of Samples 6-10

EL devices, Samples 6 through 10 were fabricated in an identical manner as Sample 1, but Inv-1 was replaced with Inv-2. The levels at which these materials were used are indicated in Table 2. The cells thus formed were tested for efficiency and color at an operating current of 20 mA/cm<sup>2</sup> and the results are reported in Table 2 in the form of output efficiency (W/A), luminance yield (cd/A), maximum wavelength ( $\lambda_{\max}$ ) of emission and CIE coordinates.

Table 2. Evaluation Results for EL devices 6-10.

Sample	Level (%)	Efficiency (W/A)	Yield (cd/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	Emission $\lambda_{\text{max}}$ (nm)	Type
6	0.50	0.031	1.58	0.168	0.160	456	Invention
7	1.00	0.030	1.76	0.172	0.190	460	Invention
8	2.00	0.029	1.85	0.177	0.214	464	Invention
9	4.00	0.027	1.98	0.188	0.255	468	Invention
10	0.00	0.035	1.58	0.164	0.136	448	Comparison

As can be seen from Table 2, all tested EL devices incorporating the invention light-emitting material exhibit blue or blue-green electroluminescence with a desired yield.

### Device Example 3 – EL Device Fabrication of Samples 11-15

An EL device (Sample 11) satisfying the requirements of the invention was constructed in the following manner:

1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO) as the anode was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CF<sub>x</sub>) hole-injecting layer (HIL) by plasma-assisted deposition of CHF<sub>3</sub>.
3. A hole-transporting layer (HTL) of *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 75 nm was then evaporated from a tantalum boat.
4. A 20 nm light-emitting layer (LEL) of 2-*tert*-butyl-9,10-di-(2-naphthyl)anthracene (TBADN), 2,5,8,11-tetra-*t*-butyl perylene (1.50 wt%), and Inv-1 (0.50%) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.

5. A 35 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) ( $\text{AlQ}_3$ ) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.

5 6. On top of the  $\text{AlQ}_3$  layer was deposited a 220 nm cathode formed of a 10:1 volume ratio of Mg and Ag.

The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

10 Additional EL devices were fabricated with different levels of Inv-1, in this case a range of 0.50% to 4.0 % of Inv-1 was found to give desirable results. Thus, EL devices, Samples 12-14, incorporating Inv-1 were fabricated in an identical manner as Sample 11 except Inv-1 was used at the levels indicated in the Table 1. Sample 15 was prepared in the same manner as Sample 1 except Inv-1 was omitted. The cells thus formed were tested for yield and color at an  
15 operating current of  $20 \text{ mA/cm}^2$  and the results are reported in Table 3. The cells were tested for stability by operating the cells at  $40 \text{ mA/cm}^2$  for 401 h at room temperature. The luminance after operating for this time relative to the initial luminance is listed in Table 3 as a percentage.

20

Table 3. Evaluation Results for EL devices 11-15.

Sample	Level (%)	Yield (cd/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	Emission $\lambda_{\text{max}}$ (nm)	Stability (%)	Type
11	0.50	2.66	0.145	0.220	464	80	Invention
12	1.00	2.05	0.153	0.230	464	83	Invention
13	2.00	2.17	0.159	0.276	468	82	Invention
14	4.00	1.97	0.172	0.308	468	76	Invention
15	0.00	2.60	0.143	0.180	460	72	Comparison

As can be seen from Table 3, the tested EL devices incorporating  
25 the invention material exhibit improved stability.

#### Device Example 4 – EL Device Fabrication of Samples 16-20

EL device, Sample 16 was fabricated in an identical manner as Sample 11, except Inv-1 was replaced with Inv-2. Thus the light-emitting layer contains 2-*tert*-butyl-9,10-di-(2-naphthyl)anthracene (TBADN), 2,5,8,11-tetra-*t*-butyl perylene (1.50 wt%), and Inv-2 (0.50%).

EL devices, Samples 17-20 incorporating Inv-2 were fabricated in an identical manner as Sample 16 except Inv-2 was used at the levels indicated in the Table 4. Sample 21 was prepared in the same manner as Sample 1 except Inv-1 was omitted. The cells thus formed were tested for efficiency and color at an operating current of 20 mA/cm<sup>2</sup> and the results are reported in Table 4. The cells were tested for stability by operating the cells at 40 mA/cm<sup>2</sup> for 413 h at room temperature. The luminance after operating for this time relative to the initial luminance is listed in Table 4 as a percentage.

Table 4. Evaluation Results for EL devices 16-21.

Sample	Level (%)	Yield (cd/A)	CIEx	CIey	Emission $\lambda_{\text{max}}$ (nm)	Stability (%)	Type
16	0.50	2.83	0.142	0.210	464	82	Invention
17	1.00	2.31	0.146	0.194	464	85	Invention
18	2.00	2.52	0.150	0.232	464	88	Invention
19	4.00	2.21	0.163	0.249	464	94	Invention
20	8.00	2.43	0.175	0.292	464	92	Invention
21	0.00	2.97	0.141	0.202	464	73	Comparison

As can be seen from Table 4, the tested EL devices incorporating the invention material exhibit improved stability.

The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference. The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

## **PARTS LIST**

101	Substrate
103	Anode
105	Hole-Injecting layer (HIL)
107	Hole-Transporting layer (HTL)
109	Light-Emitting layer (LEL)
111	Electron-Transporting layer (ETL)
113	Cathode